

"PML/Oxide/PML Barrier Layer Performance Differences Arising From Use Of UV or Electron Beam Polymerization of the PML Layers."

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Comparison of Surface Treatments of PET and PML

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ABSTRACT

PolyethyleneTerephthalate (PET) and acrylic based polymeric films deposited by the Polymer Multi-Layer (PML) method have been treated either with a corona discharge or with an e-beam. The gases employed in the corona discharge were argon, oxygen and nitrogen. The effects of the different treatments on surface topography, elemental composition and chemical changes at the surface were studied by Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). The influence of the treatments is much more profound on the linear-chain polymer PET than on the highly crosslinked PML polymeric layer. The e-beam treatment was found to be fundamentally different from the corona discharge treatments.

INTRODUCTION

Many polymeric substrate materials such as polyethylene, (PE), polypropylene (PP), and PET require some type of surface modification in order to obtain good adhesion to a variety of coatings. A large number of surface treatments have been developed over the years to achieve this goal. Among them are corona discharge, flame, remote plasma, UV, laser, and electron beam treatments. Corona discharge treatment is by far the one most widely used in industrial coatings processes and its effect has been studied extensively.¹

At the Pacific Northwest National Laboratory (PNNL) our group is working with a method of depositing acrylic polymer films in a roll-to-roll process on flexible substrates. This coatings method has been named the Polymer Multi-Layer (PML) process.^{2,4} Acrylic monomer is vacuum flash-evaporated and subsequently cured with either UV-light or an electron beam to form a solid film. This process can be used in combination with magnetron sputtering and/or e-beam evaporation to yield a variety of high quality coatings such as barriers, optical thin films, and highly reflective coatings on rough substrates.^{2,4} In all these applications, good adhesion of the PML layer to the flexible polymer substrate and good adhesion of the sputtered or e-beam evaporated layers to PML is absolutely crucial to obtain usable, high quality films.

Therefore, we have undertaken a detailed, comparative study of the influence of typical polymer surface treatments using unreactive and reactive gases and electron beam-treatment.

EXPERIMENTAL

The corona treatments and the PML coating depositions were performed in PNNL's vacuum webcoater. The hardware and the process has been discussed elsewhere.^{2,3} The thickness of the PML layer was 1 μm and the flash-evaporated monomer was cured by UV light.

Corona and e-beam treatments were each performed at two power settings. The total energy input in the corona treatments was 34 J/cm² and 8 J/cm², respectively. The gases used were argon, oxygen and nitrogen. The total energy input in case of the e-beam treatments was 40 J/cm² and 10 J/cm², respectively. The PET substrate was treated at both energies, while the PML coating was only exposed to the higher intensity. After treatment all surfaces were exposed to air, i.e. the measurements were not performed *in-situ*. X-ray Photoelectron Spectroscopy (XPS) analyses were performed in a PHI 550 XPS instrument with a double-pass cylindrical mirror analyzer. The spectra were recorded with a MgK α -anode operated at 300 W. High resolution scans were acquired at 25 eV and 0.05 eV step size. They were charge corrected to the neutral hydrocarbon C1s peak occurring at 284.6 eV. The take-off angle with respect to the surface was 60° in all cases which translates to an approximate information depth of 3 nm. Atomic Force Microscopy (AFM) images were obtained using a Digital Instruments Nanoscope III instrument. All of the AFM images were acquired in air using the contact mode.

RESULTS AND DISCUSSION

AFM images of the untreated and treated PET substrate and the untreated and treated PML substrate are depicted in Figure 1a-k. Only the surfaces treated at the higher energy inputs are shown. Section analyses which give more quantitative information on surface features are depicted in Figure 2 and the calculated root-mean-square (RMS) surface roughness values of all the films are given in Table I.

From Figures 1 and 2 it is obvious that the changes in surface topography depend largely on the nature of the treatment and on the gases used. It can also be seen that the changes in the surface topographical features are much more pronounced in the case of PET than in the case of PML. An untreated PET surface exhibits a surface showing a fairly regular pattern of spikes of approximately 35 nm in height. These are caused by the manufacturer's surface treatment and help to minimize tack. The observed changes in these features due to different surface treatment provide a convenient way of comparing different treatments.

With the reactive gases, especially oxygen, the surface roughness of the PET increases with increasing energy input. In the case of nitrogen, the original surface features are still observable. Oxygen, however, seems to have completely abraded these features and then changed the surface topography, causing new, more closely spaced spikes with a height of approximately 60 nm to appear. The RMS surface roughness for the high intensity oxygen treatment is the only one considerably higher than the one observed for the untreated PET surface. In the case of the argon plasma the surface also changes considerably. The original spikes get abraded and new, more densely spaced, features of lower height appear causing the RMS surface roughness to decrease. In the case of the e-beam treatment, no new features become apparent. The RMS surface roughness also decreases with increasing energy input but this is caused by abrading the original spikes and not the formation of smaller, more dense surface features as it was the case with the argon discharge.

The untreated 1 μ m thick PML film surface demonstrates impressively the smoothing capabilities of this coating process and has been alluded to in previous publications.^{2,4} None of the surface features of the PET substrates have been retained and the RMS surface roughness dropped by over two orders of magnitude from 13.2 nm to 0.1 nm.

Treatment of this surface with an argon discharge or e-beam does not change its topography or roughness to any appreciable extent. Only discharges from the

reactive gases nitrogen and oxygen seem to have an effect on surface topography and roughness of the PML coating. Oxygen discharges seem to produce densely spaced spikes of approximately 5 nm height, while nitrogen plasmas give rise to broader, less densely spaced spikes which seem to have approximately the same height as the ones produced in the oxygen discharge.

The observed difference of the influence of the treatments on the surface topographies of PET and PML can be explained with their structural differences. While PET consists of long polymer chains, which readily undergo chain scission reactions upon treatment to form low molecular weight material at the surface which can be removed easily.^{1,5} Figure 3 shows the molecular structure of PET and the most likely chain scission points.

Figure 3. PET and the most likely points where its structure can be attacked by a surface treatment

In contrast to this, PML has a highly crosslinked, very rigid polymeric structure. This high crosslink density is caused by the high concentration of diacrylates in the monomer composition. Upon polymerization these monomers form a 3-dimensional network which is very stable. The polymer backbone is thus a purely hydrocarbon based crosslinked net which is much harder to attack than the polymer chains in PET. Therefore, the influence of energetically equivalent surface treatments on the PML layer's topography can be expected to be much less pronounced than in the case of PET.

Substantial differences in surface topography and RMS surface roughness can be seen for both PET and PML depending on the type of gas used in the corona discharge, i.e. oxygen and nitrogen are different from argon. This becomes understandable in light of the fundamental interactions that can occur between a plasma and a non-polymerizable gas, namely etching, implantation and radical formation.⁶ All these reactions

are conceivable with any of the treatments used. Oxygen and nitrogen can also react with the low molecular weight material that is created by the above mentioned mechanisms to form highly volatile or gaseous compounds, e.g. CO₂, amines. Thus, in addition to the physical etching process, chemical processes help in removing surface material. The effect can be expected to become much more pronounced with higher gas and/or energy densities.

Table I
RMS values of treated and untreated PET and PML

Sample	Treatment	RMS (nm)
PET	—	13.2
PET	Ar, 8 J/cm ²	7.9
PET	Ar, 34 J/cm ²	5.2
PET	EB, 10 J/cm ²	6.8
PET	EB, 40 J/cm ²	4.7
PET	N ₂ , 8 J/cm ²	2.5
PET	N ₂ , 34 J/cm ²	9.6
PET	O ₂ , 8 J/cm ²	10.6
PET	O ₂ , 34 J/cm ²	20.2
PML	—	1
PML	Ar, 34 J/cm ²	1
PML	EB, 34 J/cm ²	1
PML	O ₂ , 34 J/cm ²	2
PML	N ₂ , 34 J/cm ²	2

The elemental compositions of the differently treated surfaces, as determined by XPS, are shown in Table II. It is noteworthy that the PET substrate does not exhibit the theoretical O/C ratio of 0.29/0.71. It seems that the surface is oxygen enriched. This is caused most likely by the manufacturer's surface treatment already mentioned previously.

For all treatments of PET surfaces, Table II shows a difference in elemental composition between the low and the high energy input. Except for the e-beam treatment, the O/C ratio increases with increasing energy. For the low energy e-beam treatment no changes in the elemental composition of the surface can be detected, while the high energy treatment causes the surface to become much more hydrophobic. This is the only case in the whole study where a high energy treatment actually *decreases* the amount of functional

groups on the surface. Another surprising observation that can be made from Table II is that the high energy argon treatment results in a higher O/C ratio than the high energy oxygen treatment. The nitrogen discharge causes the imbedding of nitrogen into the PET structure. For the low energy treatment, the nitrogen simply seems to replace the oxygen, while the high energy treatment also causes an uptake of oxygen. For both energy inputs the amount of nitrogen that is imbedded into the PET substrate is comparable. In the case of the oxygen discharge, a higher energy input does not increase the O/C ratio appreciably. Chemical information on the presence of functional groups can be obtained from a thorough analysis of the shapes of the C1s and the O1s peaks. Due to space constraints they are not shown here. In general, it can be said that the ester group (-COOR) decreases in every surface treatment. The high intensity e-beam treatment totally removes it from the PET surface. The neutral hydrocarbon component (C-C, C-H, C=C) decreases for every plasma treatment, only the high intensity e-beam actually increases it. The C-O-C and/or C-O-H component of the C1s peak increases in every case. New functional groups that are formed are carboxylic acid (-COOH) and keto- and/or aceto ((RH)C=O, (RR)C=O)) groups. The C1s and N1s spectra in case of the nitrogen discharge show evidence for C-N containing groups.

The effect of the treatments on the elemental composition of the PML coatings is very minor even though they have been performed at the higher of the two energy intensities. Only oxygen and to a very minor extent nitrogen discharges change the elemental composition noticeably. Both, the argon plasma and the e-beam which had the most pronounced and opposite effects in the PET treatments show almost no changes at all when applied to the PML layers. Analyses of the C1s and the O1s indicate an increase in the C-O-C and/or C-O-H component of the C1s peak region. No decrease in the ester functionality can be detected.

The XPS analyses corroborate the AFM measurements. The elemental composition of PET is easily changed and new functional groups and elements can be introduced readily by the plasma treatments. The elemental composition in the case of the PML coatings is much harder to alter with surface treatments. Only oxygen seems to be capable of changing the surface chemistry to an appreciable amount. The reason for this has already been pointed out in the section that deals with the discussion of the AFM data.

A high intensity e-beam treatment renders the surface much more hydrophobic. It is surprising that the low

intensity e-beam does not alter the PET surface at all. In case of the e-beam treatment there seems to be a certain energy threshold below which no effect on the surface composition is detectable. Further experiments are necessary to substantiate this claim. Use of the high intensity argon plasma of PET results in the highest O/C ratio of all treatments. Since the samples have been exposed to air prior to the XPS measurements this observation can be explained with a very high amount of radical formation on the surface caused by the argon plasma. When these radical sites are exposed to the atmosphere they readily react with residual oxygen and water.

Table II

Elemental composition of treated and untreated PET and PML as determined by XPS

Sample	Treatment	C	O	N
PET	—	0.60	0.40	
PET	Ar, 8 J/cm ²	0.54	0.46	
PET	Ar, 34 J/cm ²	0.53	0.67	
PET	EB, 10 J/cm ²	0.60	0.40	
PET	EB, 40 J/cm ²	0.83	0.17	
PET	N ₂ , 8 J/cm ²	0.66	0.24	0.10
PET	N ₂ , 34 J/cm ²	0.58	0.32	0.10
PET	O ₂ , 8 J/cm ²	0.52	0.48	
PET	O ₂ , 34 J/cm ²	0.50	0.50	
PML	—	0.70	0.30	
PML	Ar, 34 J/cm ²	0.74	0.29	
PML	EB, 34 J/cm ²	0.72	0.28	
PML	O ₂ , 34 J/cm ²	0.59	0.41	
PML	N ₂ , 34 J/cm ²	0.68	0.29	0.03

CONCLUSIONS

PML coatings routinely exhibit RMS surface roughness values of 0.1 nm or less. Their smoothing capability even on very rough substrates is outstanding and can only be equaled by an extremely expensive surface polish.

Surface treatments of the linear-chain polymer PET have much higher effects on its surface topography and composition than treatment of the highly crosslinked PML surface.

Reactive gases like oxygen and nitrogen have a substantially higher impact on the surface

topography and roughness of both PET and PML when compared to treatments using inert gases like argon. This can be explained by their ability to form volatile compounds with low molecular weight species in addition to the surface etching.

Oxygen is the only gas of those studied that can noticeably change the elemental composition of the PML surface. Thus, it is the gas of choice for adhesion enhancement to PML surfaces.

Contrary to corona treatments, high intensity e-beam treatments result in a much more hydrophobic surface. This could interfere with adhesion of metals, metal-oxides and polar polymers.

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